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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 03 FEB 2005



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Applicant's or agent's file reference P.CRGL.01WO	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/12074	International filing date (day/month/year) 24.10.2003	Priority date (day/month/year) 25.10.2002
International Patent Classification (IPC) or both national classification and IPC G01N23/225		
Applicant CENTRE DE RECHERCHE PUBLIC-GABRIEL LIPPMANN et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.
  - ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:
  - I ☒ Basis of the opinion
  - II ☐ Priority
  - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV ☒ Lack of unity of invention
  - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI ☐ Certain documents cited
  - VII ☐ Certain defects in the international application
  - VIII ☐ Certain observations on the international application

Date of submission of the demand  15.03.2004	Date of completion of this report  03.02.2005
Name and mailing address of the international preliminary examining authority:   European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer  Wulveryck, J-M  Telephone No. +31 70 340-3689 

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. **PCT/EP 03/12074**

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*);

**Description, Pages**

1-35 as originally filed

**Claims, Numbers**

1-17 received on 11.01.2005 with letter of 10.01.2005

**Drawings, Sheets**

1/10-10/10 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☒ the claims, Nos.: 18-23  
☐ the drawings, sheets:

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5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**IV. Lack of unity of invention**

1. In response to the invitation to restrict or pay additional fees, the applicant has:

- ☐ restricted the claims.  
☐ paid additional fees.  
☐ paid additional fees under protest.  
☐ neither restricted nor paid additional fees.

2. ☒ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- ☐ complied with.  
☒ not complied with for the following reasons:

**see separate sheet**

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- ☒ all parts.  
☐ the parts relating to claims Nos. .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-17
	No: Claims	
Inventive step (IS)	Yes: Claims	1-17
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-17
	No: Claims	

2. Citations and explanations

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**see separate sheet**

**Re Item IV**

**Reasoned statement with regard to unity of invention**

Reference is made to the following document:

D1: T. WIRTZ, B. DUEZ, H. -N. MIGEON, H. SCHERRER: "Useful yields of  $Mcs^+$  and  $Mcs^{2+}$  clusters: a comparative study between the Cameca IMS 4f and the Cation Mass Spectrometer" INTERNATIONAL JOURNAL OF MASS SPECTROMETRY, vol. 209, 2001, pages 57-67, XP001197305

The claims do not satisfy the requirement of unity of invention (Rule 13 PCT). The reasons are as follows:

1. The apparatus for carrying out the method of independent claim 1 and the apparatus defined by independent claim 13, only have in common an apparatus comprising a neutral caesium ( $Cs^0$ ) deposition column capable of delivering an collimated adjustable and stable stream of pure neural caesium . This concept is however already known from XP001197305 (D1).

2. The independent claims can be grouped according to their special technical features apart from these known concepts:

I. Claim 1 directed towards a method for optimising the deposited  $Cs^0$  concentration only by adjusting the ratio ( $\tau = v_{er}/v_D$ ), between the erosion rate ( $v_{er}$ ) and the  $Cs^0$  deposition rate ( $v_D$ ).

The problem solved is the monitoring of  $Cs^0$  concentration simply by adjusting a general parameter without modifying the bombardment conditions.

II. Claim 13 directed towards a collimation means equipped with temperature control means.

This solves the problem of the condensation of  $Cs^0$  on the deposition column and its obturation.

3. There is no feature common to these two groups, which could be considered as a special technical feature within the meaning of PCT Rule 13.2, second sentence. Thus no technical relationship within the meaning of PCT Rule 13 between the two groups of inventions can be seen.

4. Consequently it appears that, a posteriori, claims 1 and 13 do not satisfy the requirements of unity of invention within the meaning of PCT Rule 13.

**Re Item V**

**Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1 INDEPENDENT CLAIM 1**

- 1.1 The document D1 is regarded as being the closest prior art to the subject-matter of claim 1, and shows (see page 58) an apparatus working according a method in which in situ deposition of neutral caesium ( $\text{Cs}^0$ ) is used to modify the electronic properties of a surface to analytical ends. The deposition of the neutral caesium is carried out using a column (i.e. collimation means) and is adjustable. The apparatus disclosed in D1 comprises also means for bombarding the sample surface simultaneously.
- 1.2 The subject-matter of claim 1 differs from this known apparatus in that the optimised deposited  $\text{Cs}^0$  concentration is chosen only by adjusting the ratio between the erosion rate and the deposition rate.

The subject-matter of claim 1 is therefore new (Article 33(2) PCT).

- 1.3 The problem to be solved by the present invention may be regarded as monitoring the deposited  $\text{Cs}^0$  concentration simply by adjusting a general parameter without modifying the bombardment conditions.
- 1.4 The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons: the erosion rate being fixed, the ratio is modified by simply varying the deposition rate, i.e. by varying the heating power of the evaporation block.

**2 INDEPENDENT CLAIM 13**

- 2.1 The document D1 is regarded as being the closest prior art to the subject-matter of claim 13, and shows (see page 58) an apparatus in which in situ deposition of neutral caesium ( $\text{Cs}^0$ ) is used to modify the electronic properties of a surface to analytical ends. The deposition of the neutral caesium is carried out using a column (i.e. collimation means) and is adjustable. The apparatus disclosed in D1 comprises also

means for bombarding the sample surface simultaneously.

- 2.2 Claim 13 differs from this known apparatus in that it defines a collimation means equipped with temperature control means.

The subject-matter of claim 13 is therefore new (Article 33(2) PCT).

- 2.3 The problem to be solved by the present invention may be regarded as preventing the condensation of neutral caesium on the deposition column and its obturation.

- 2.4 The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons: by heating the collimation means, the neutral caesium can not stick to it, and then any risk of obturation is prevented..

### **3 DEPENDENT CLAIMS 2-12, 14-17**

Claims 2-12, 14-17 are dependent, respectively, on claim 1 and claim 13 and as such also meet the requirements of the PCT with respect to novelty and inventive step.

CLAIMS

1. Method for modifying the electronic properties of a surface to analytical ends, characterised in that it comprises in situ deposition of neutral cesium (Cs<sup>0</sup>), under ultra-high vacuum, said neutral cesium being enabled in the form of a collimated adjustable stream.

2. Method according to Claim 1, characterised in that the stream of Cs<sup>0</sup> is provided and collimated in a column by means of:

- a temperature adjustment of an evaporator comprising a metallic cesium reservoir, and/or
- an aperture control of a motorised obturator located in the path of the cesium stream.

3. Method according to Claim 1 or 2, characterised in that said Cs<sup>0</sup> deposition is simultaneously accompanied by a primary bombardment comprising electrons and/or ions or neutral atoms or groups of atoms, or by an X-ray irradiation, intended to induce an emission of a beam of particles for analysis, out of the surface.

4. Method according to anyone of Claims 1 to 3, characterised in that it is coupled to static or dynamic Secondary Ion Mass Spectroscopy (SIMS), preferably operating in the MCs<sub>x</sub><sup>+</sup> mode (x = 1, 2).

5. Method according to Claim 4, characterised in that the deposition rate of Cs<sup>0</sup> is continuously adjustable in the range from 0 to 10 Å/s, corresponding about to 0 - 4 monolayers per second.

6. Method according to anyone of Claims 1 to 3, characterised in that it is coupled to electron spectroscopy.

7. Method according to Claim 6, characterised in that electron spectroscopy is selected from the group consisting of Auger Electron Spectroscopy

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(AES), Electron Energy Loss Spectroscopy (EELS), X-Ray Photoemission Spectroscopy (XPS) and Ultraviolet Photoemission Spectroscopy (UPS).

8. Method according to anyone of Claims 3 to 5, characterised in that the secondary beam for analysis comprises secondary electrons and/or  $Cs_x^{n+}$  and/or  $MCs_x^{n+}$  positive clusters and/or  $M^{n-}$  negative ions and/or  $M^{m+}$  positive ions, M being a constituent of the sample material made of an atom or a group of atoms (n, m integers).
9. Method according to Claim 8, characterised in that the sputtering and Cs introduction phases are decoupled during analyses in the  $MCs_x^+$  mode, in a simultaneous optimisation of deposited Cs concentration and analytical characteristics, such as the depth resolution.

10. Method according to Claim 8 or 9, characterised in that the depth resolution solely depends on the bombardment conditions for the analysis.

11. Method according to anyone of Claims 8 to 10, characterised in that it further enables a stream of a chemical element other than Cs, evaporated under ultra-high vacuum, to create secondary emission for analytical purposes of  $M_1M_2^{n+}$  clusters or  $M_2^{m-}$  ions or  $M_2^{m+}$  ions (n, m integers) or electrons, wherein  $M_1$  and  $M_2$  are respectively the atoms or groups of atoms constituted by the chemical element other than Cs and the atoms or groups of atoms from the sample.

12. Method according to anyone of Claims 8 to 11, characterised in that the sole adjustable deposition rate of  $Cs^0$  or a chemical element other than Cs to an optimised value enables to optimise the intensity of the secondary particles emitted by the sample.

13. Method according to anyone of Claims 8 to 12, characterised in that the reservoir temperature range

is maintained between 70 and 90 °C, corresponding to a pressure range from  $1.10^{-4}$  to  $4.10^{-4}$  mbar and in that the stability of the deposition rate is about 2% over 60 minutes.

5 14. Method according to anyone of Claims 8 to 13, characterised in that, under bombardment analysis mode, the deposited  $Cs^0$  concentration is solely related to the respective Cs and sample densities ( $\rho_{Cs}, \rho_M$ ), to the sputtering yield in the given bombardment conditions (Y) 10 and to the ratio between the  $Cs^0$  erosion ( $v_{er}$ ) and the deposition ( $v_D$ ) rate ( $\tau = v_{er}/v_D$ ).

15 15. Method according to Claim 14, characterised in that the useful yield, i.e. the sensitivity, of the secondary emission species, preferably  $M^{n-}$ ,  $M^{m+}$ , and still more preferably  $Cs_x^{n+}$  and  $MCs_x^{n+}$ , is approximately solely related to said ratio ( $\tau$ ) and not to the respective erosion and deposition rate taken individually and in that the secondary signal is optimisable by adjusting the  $Cs^0$  deposition rate to attain 20 an optimum value of said ratio ( $\tau$ ).

16. Method according to anyone of Claims 8 to 15, characterised in that the stream of  $Cs^0$  is automatically and continuously adapted via the obturator.

25 17. Energy and/or mass analyser instrument for carrying out the method according to anyone of the preceding Claims 1 to 16, characterised in that it comprises a neutral cesium ( $Cs^0$ ) deposition column capable of delivering an adjustable and stable stream of pure neutral cesium, said column being preferably usable 30 simultaneously with a primary bombardment or a primary irradiation column.

18. Instrument according to Claim 17, preferably a static or dynamic secondary ion mass

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spectrometry (SIMS) instrument, characterised in that it comprises a primary bombardment column and a secondary column equipped with secondary ion extraction means, a mass spectrometer, preferably of the type TOF (Time-Of-Flight),  
5 quadrupolar or with magnetic sector and ion detection means.

19. Neutral cesium column usable in an instrument according to Claim 17 or 18, characterised in that said neutral cesium column comprises an evaporation  
10 block (1) including a reservoir (5) filled with pure metallic cesium, equipped with temperature control means (6,7), prolonged by a tube (2,11) up to a gun end piece (13) located close to the sample and equipped with beam collimation means (12).

15 20. Neutral cesium column according to Claim 19, characterised in that said beam collimation means comprise a motorised continuously adjustable obturator (12), preferably comprising a rotary disk using a slit of continuously variable width (16), said disk being driven by  
20 a stepper motor (17).

21. Neutral cesium column according to Claim 19 or 20, characterised in that, at the operation temperature, the neutral cesium ( $\text{Cs}^0$ ) is in liquid state and the evaporation block (1) lies with an inclination  
25 angle such as said liquid remains in the bottom of the reservoir (5) under gravity effect.

22. Neutral cesium column according to anyone of Claims 19 to 21, characterised in that said tube (2, 11) and gun end piece (13) equipped with beam collimation means  
30 (12) are further equipped with temperature control means (8,14,15) for preventing condensation and obturation risks.

23. Neutral cesium column according to anyone of Claims 19 to 22, characterised in that the evaporator block (1) is located in an external part which can be

isolated from the main chamber (3) of the instrument by means of a gate valve (4) and capable of being separately pumped and vented.